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## THE TEMPORAL DEPENDENCE OF ADHESION JOINING STRENGTH: THE DIFFUSIVE MODEL

*Key words: polystyrene, adhesion, strength, fractal analysis, anomalous diffusion.*

*The quantitative model of the dependence of adhesion contact shear strength on its formation duration was proposed, which uses fractal analysis and strange (anomalous) diffusion notions. This model gives a clear physical picture of contact formation and allows precise enough estimations of adhesion joining strength.*

*Ключевые слова: полистирол, адгезионная прочность, фрактальный анализ, anomalous diffusion.*

*Предложена количественная модель зависимости адгезионной прочности от времени формирования контакта с использованием рекурсивного анализа и аномальной диффузии. Эта модель дает четкую физическую картину формирования контакта и позволяет достаточно точно оценить адгезионные характеристики.*

### 1. Introduction

At present the general law – governed nature is well-known: adhesional contact formation duration increasing at other equal conditions results in its strength enhancement [1, 2]. As a rule, this effect is explained by macromolecular coils diffusion in boundary layer of samples, forming adhesional contact [3]. However, such explanation has usually a qualitative character. Therefore the present work purpose is the development of the quantitative model adhesional contact strength temporal dependence. Within the frameworks of fractal analysis and anomalous (strange) diffusion conception on the example of amorphous polymer – polystyrene (PS) [1].

### 2. Experimental

Amorphous PS ( $M_w=23 \times 10^4$ ,  $M_w/M_n=2.84$ ), obtained from Dow Chemical (USA) was used. The glass transition temperature  $T_g$  was measured using Perkin-Elmer DSC-4 differential scanning calorimeter, at a heating rate of 20 K/min ( $T_g=376$  K for PS) [2]. For adhesional joinings formation two samples with width of 5 mm were bonded in a lap-shear joint geometry with the area of  $5 \times 5$  mm<sup>2</sup>, using a Carver laboratory press at constant temperature and pressure of 0.8 MPa. Division boundaries PS-PS were healed during 10 min and 24 h within the range of temperatures of 335–373 K – in all cases below glass transition temperature. Mechanical tests of the formed contacts were conducted at temperature 293 K on an Instron tensile tester, Model 1130 at tension rate of  $3 \times 10^{-2}$  m/s with shear strength determination in the contact zone (or on division boundary) [1, 2].

### 3. Results and Discussion

As it is known [4], within the frameworks of fractal analysis shear strength  $\tau_c$  of adhesional joining is described by the following general equation:

$$\ln \tau_c = A \ln N_c - B, \quad (1)$$

where  $A$  and  $B$  are constants, which can be changed depending on polymer nature, temperature, testing specific conditions and so on,  $N_c$  is macromolecular coils contacts number, which is determined as follows [5]:

$$N_c \sim R_g^{D_{f_1} + D_{f_2} - d}, \quad (2)$$

where  $R_g$  is a macromolecular coil gyration radius,  $D_{f_1}$  and  $D_{f_2}$  are fractal dimensions of the coils structure,

forming autohesional bonding,  $d$  is dimension of Euclidean space, in which a fractal is considered (it is obvious, that in our case  $d=3$ ).

For the autohesion case  $D_{f_1} = D_{f_2} = D_f$  and  $d=3$  the equation (2) is simplified up to:

$$N_c \sim R_g^{2D_f - 3}. \quad (3)$$

Let us consider estimation methods of the parameters, included in the equation (3), i.e.  $D_f$  and  $R_g$ . For the dimension  $D_f$  estimation the following approximated technique will be used, which consists in the following. As it is known [7], between  $D_f$  and structure dimension  $d_f$  of linear polymers in the solid state the following intercommunication exists:

$$D_f = \frac{d_f}{1.5}. \quad (4)$$

$d_f$  estimation can be conducted according to the formula [6]:

$$d_f = 3 - 6 \left( \frac{\Phi_{cl}}{SC_\infty} \right)^{1/2}, \quad (5)$$

where  $\Phi_{cl}$  is a relative fraction of local order domains (clusters),  $S$  is a macromolecule cross-sectional area,  $C_\infty$  is characteristic ratio, which is an indicator of polymer chain statistical flexibility [8].

$\Phi_{cl}$  value was estimated according to the following percolation relationship [6]:

$$\Phi_{cl} = 0.03(T_g - T)^{0.55}, \quad (6)$$

where  $T_g$  and  $T$  are temperatures of glass transition and autohesional contact formation, respectively.

For PS  $C_\infty=9.8$  [9],  $S=54.8 \text{ \AA}^2$  [10]. Further the macromolecular coil gyration radius  $R_g$  was calculated as follows [11]:

$$R_g = l_0 \left( \frac{C_\infty M_w}{6m_0} \right)^{1/2}, \quad (7)$$

where  $l_0$  is the length of the main chain skeletal bond, which is equal to 0.154 nm for PS [9],  $m_0$  is the molar mass per backbone bond, which is equal to 52 for PS [11].

Let us note the important methodological aspect. At  $R_g$  value calculation according to the equation

(7) value  $C_\infty$  was accepted as a variable one and calculated according to the following equation [6]:

$$C_\infty = \frac{2d_f}{d(d-1)(d-d_f)} + \frac{4}{3}. \quad (8)$$

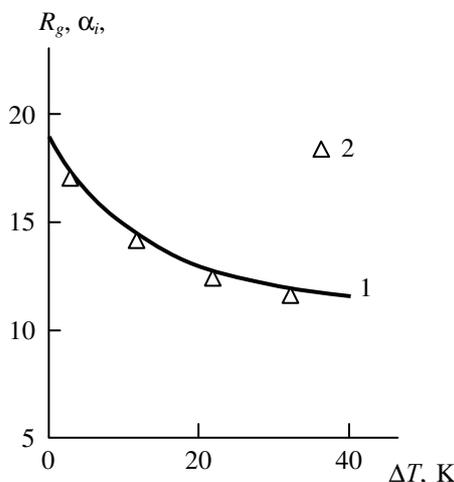
The constants  $A$  and  $B$  in the equation (1) for PS are equal to 2.15 and 6.0, respectively [12].

As it is known [11], at  $M_w > 12M_e$  (where  $M_e$  is molecular weight of a chain part between macromolecular entanglements) the boundary layer thickness  $\alpha_i$  in the autohesion case can be determined according to the formula [11]:

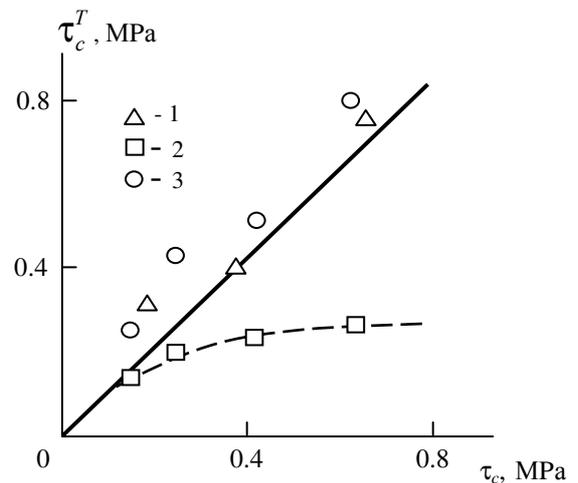
$$\alpha_i = l_0 \left( \frac{12C_\infty M_e}{6m_0} \right)^{1/2}. \quad (9)$$

In PS case  $M_e = 18000$  [11], i.e. the indicated above condition  $M_w > 12M_e$  is fulfilled and the equation (9) can be used for  $\alpha_i$  value estimation. In Fig. 1 the comparison of macromolecular coil gyration radius  $R_g$ , calculated according to the equation (7), and the boundary layer thickness  $\alpha_i$ , calculated according to the formula (9), is adduced. As one can see, at contact formation duration  $t = 10$  min  $\alpha_i$  value reaches  $R_g$  value in PS case. Let us also note, that the equation (9) does not assume  $\alpha_i$  dependence on contact formation duration  $t$ , although the dependence  $\tau_c(t)$  exists [1]. This circumstance provides boundary layer structure change for autohesional joining at  $t > 10$  min.

In Fig. 2 the comparison of experimental  $\tau_c$  and calculated according to the equation (1)  $\tau_c^T$  autohesional joining PS-PS shear strength values at the indicated above conditions is adduced. As one can see, if for  $t = 10$  min the theory and experiment good correspondence is observed, then for  $t = 24$  hours such correspondence is absent – the values  $\tau_c^T$  are essentially smaller than the experimentally obtained ones. As it was noted above, this effect was due to boundary layer structure change in virtue of proceeding in it macromolecular coils diffusion processes. Let us consider the indicated processes within the frameworks of anomalous (strange) diffusion conception [13].



**Fig. 1 - The dependences of macromolecular coil gyration radius  $R_g$  (1) and boundary layer thickness  $\alpha_i$  (2) on autohesional joining glass transition and formation temperatures difference  $\Delta T = T_g - T$  for PS**



**Fig. 2 - The comparison of experimental  $\tau_c$  and calculated according to the equation (1)  $\tau_c^T$  shear strength values of autohesional joining for PS. The joining formation duration  $t = 10$  min (1) and 24 hours (2, 3). The calculation of dimension  $d_f$  according to the equation (5) (1, 2) and (13) (3)**

The basic equation of this conception can be written as follows [14]:

$$\langle r^2(t) \rangle^{1/2} = D_{gen} t^\beta, \quad (10)$$

where  $\langle r^2(t) \rangle^{1/2}$  is mean-square displacement of a diffusible particle (the size of region, visited by this particle),  $D_{gen}$  is generalized diffusivity,  $\beta$  is diffusion exponent. For the classical case  $\beta = 1/2$ , for the slow diffusion -  $\beta < 1/2$  and for the fast one -  $\beta > 1/2$ . The condition  $\beta \neq 1/2$  is the definition of anomalous (strange) diffusion.

The border value for slow and fast diffusion processes is the condition  $d_f = 2.5$  [13]. Since for the considered in the present work PS samples  $d_f \geq 2.88$ , then all proceeding in them diffusion processes are slow ones. The exponent  $\beta$  value is connected with the main parameter in a fractional derivatives theory (fractional exponent  $\alpha$ ) by the following relationship [13]:

$$\beta = \frac{1 - \alpha}{2}. \quad (11)$$

In its turn, the fractional exponent  $\alpha$  is determined according to the equation [13]:

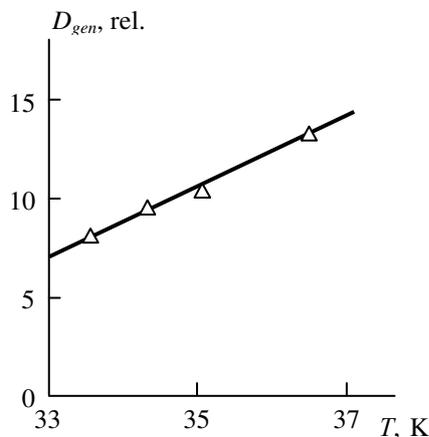
$$\alpha = d_f - (d - 1). \quad (12)$$

The equations (11) and (12) combination allows to obtain direct interconnection between rate (intensity) of diffusive processes in the autohesional joining border layer, characterized by exponent  $\beta$ , and the polymer structure, characterized by dimension  $d_f$ :

$$\beta = \frac{d - d_f}{2}. \quad (13)$$

It is obvious, that in the autohesion case the value  $\langle r^2(t) \rangle^{1/2}$  will be equal to  $\alpha_i$  and then generalized diffusivity  $D_{gen}$  at  $t = 10$  min in relative units according to the equation (10) can be determined. Further the exponent  $\beta$  for  $t = 24$  hours can be determined according to the same equation and the dimension  $d_f$  of boundary layer structure for the same conditions from the equa-

tion (13) can be calculated. In Fig. 3 the dependence of  $D_{gen}$  on autohessional contact formation temperature  $T$  for PS is adduced. As it was to be expected from the most common considerations [13, 14],  $D_{gen}$  increasing at  $T$  growth is observed.



**Fig. 3 - The dependence of generalized diffusivity  $D_{gen}$  on autohessional joining formation temperature  $T$  for PS**

Let us note, that the obtained according to the equation (13)  $d_f$  values for  $t=24$  hours proved to be higher than a the ones calculated according to the equation (5) ( $d_f=2.931-2.950$  and  $d_f=2.878-2.914$ , respectively), that was expected. Then with the described above technique usage (the equations (1), (3), (4) and (13)) the values of autohessional contact shear strength  $\tau_c^t$  were calculated, the comparison of which with the corresponding experimental values  $\tau_c$  is adduced in Fig. 2. As one can see, the consideration of autohessional joining boundary layer structure change, which is due to the proceeding in it macromolecular coils anomalous (strange) diffusion processes allows to improve essentially the theory and experiment correspondence. But the main merit of the proposed model is a clear physical picture of autohessional joining shear strength temporal dependence causes.

#### 4. Conclusions

In the present paper the quantitative model of the autohessional joining shear strength dependence on

its formation duration was proposed. This model uses notions of fractal analysis and anomalous (strange) diffusion conception. The indicated model application gives a clear physical picture of the observed effect: the obtained experimentally shear strength enhancement is due to boundary layer structure change owing to macromolecular coils diffusion. This model allows also precise enough estimations of autohessional joining strength.

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